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REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burgen for this rollection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources. Jathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden. Its Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204. Arington, VA. 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC. 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE Aug. 15, 1994 3. REPORT TYPE AND DATES COVERED

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4. TITLE AND SUBTITLE

"Synthesis & Structural Properties of New Metallic

5. FUNDING NUMBERS

6. AUTHOR(S)

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DAAL03-91-G-0009

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Virginia Department of Physics/Department of Materials Scrence Charlottesville, VA 22901

Phases Exhibiting Non-Crystallographic Symmetries"

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office

P. O. Box 12211

27709-2211 Research Triangle Park, NC

ONSORING/MONITORING GENCY REPORT NUMBER

ARO28067.18-MS

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION / AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

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13. ABSTRACT (Maximum 200 words)

DTIC QUALITY INSPECTED 5

In carrying out research on aluminum-glasses ($A\ell$ -glasses), several unusual results are found: (i) Submillimeter dutile glassy ribbons are obtained. (ii) Significant enhancement in the tensile strength is measured in Al-glass ribbons with Al nanocrystallites embedded in them. (iii) Deformation induced crystallization within the shear bands is observed for the first time. (iv) Strong Al-transition metal interaction is inferred from x-ray and neutron diffraction measurements. These results have added to our understanding of formation and microstructure-mechanical effect relationships of metal-glasses, and also to the technological values of these materials. We have begun to apply our findings to the synthesis and studies of bulk metallic-glass and nanocrystalline alloys. Thus far, we have succeeded in making subcentimeter glasses based on rare-earths and magnesium-tin, nanocrystalline alloys based on refractory metals via conventional casting, and as well as, centimeter Al-glass button via consolidation of amorphous powders obtained by ball-milling. In collaboration with Professor T. Egami at U. Penn., a method for obtaining two-dimensional atomic pair distribution is developed to unravel the structure of decagonal crystals. The new method will be applied to study layered materials.

14. SUBJECT TERMS Submillimeter aluminum-glass ribbons, subcentimeter 15. NUMBER OF PAGES glassy and nanocrystalline alloys, mechanical properties, structural studies, decagonal crystals.

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED

20. LIMITATION OF ABSTRACT

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Synthesis and Structural Properties of New Metallic Phases Exhibiting Non-Crystallographic Symmetries

Statement of the problem studied:

The objectives of our research are to synthesize new aluminum-based metallic glasses and quasicrystalline alloys, to investigate their atomic-scale structures, and to study their thermal stability and formation in order to shed light on the unusual formability of the new materials. Structures of the new materials are studied by x-ray, electron, and neutron diffraction, including that of high-resolution diffraction. The structure-property relationships in systems of technological importance are also being

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investigated.

Summary of the most important results:

(1) Unfolding the atomic-scale structure of decagonal crystal -

In collaboration with Professor T. Egami (U. Penn), a technique for carrying out 2-dimensional structural analysis in layered structure is developed. Pair distribution function (PDF) in 2-d is obtained for the first time. The x-ray measurement was carried out on decagonal crystal of AlCuCo with a positive sensitive detector (PSD) placed perpendicular to the diffraction plane. With the PSD, we were able to collect the Bragg intensities from the sub-layers of the quasiperiodic planes. The results are found to agree well with a structural model for the decagonal crystal based on aggregation of clusters proposed by S. Burkov. This finding establishes the atomistic structure of a 2-d quasicrystal. Perhaps even more important is that the technique developed will provide a very powerful tool for investigating 2-d disordered systems.

(2) Investigation of criteria for glass formation -

In an effort to understand the unusual vitrification of Al-alloys that can form submillimeter ribbons and Mg-alloys that can form millimeter rods, several ternary and quaternary systems have been mapped with respect to glass formability. The latter is measured by the maximum thickness of

amorphous ribbons obtainable by single-roller melt spinning. For the $A\ell$ -alloys, typical compositions are $A\ell$ -TM1-TM2-RE, where TM=transition metal, RE=rare earth including Y; the Mg-alloys are Mg-(Cu,Ni)-X where X is Zn and other polyvalent elements. Thus, the chemistry of the alloys studied involves three types of atomic characters. Clearly, strong hybridization of s and d orbitals is prominent between them. It is found that glass formability is optimized in the $A\ell$ -Fe-Ni-Gd and Mg-Cu-Sn systems. Our study has provided the first test for our conjecture that strong and competing atomic interactions brought about by the diverse types of elements can lead to "confusions" in the atomic order, thus favoring vitrification. In comparison, previous criteria for good glass formation are more empirical, mainly they revolve around the mismatch in atomic size. It is inferred that improvement in the vitrifiability of high-strength and good corrosion resistance light-metal glasses leading to samples of larger dimensions can be expected in systems that involve more than three atomic characters.

(3) Synthesis of bulk metallic glasses by conventional casting -

We have developed a casting technique for making bulk samples directly from the melt. There is a preliminary success in obtaining bulk metallic glasses of some magnesium-based alloys. Samples are in the form of 2 mm-diameter rods. We have begun to explore the formation of bulk glasses in the rare-earth and refractory-metal based systems. To carry out the search, we employ the electronic-factor principle mentioned above as our guide. Bulk Nd-Al-TM metallic-glass rods with diameters up to 6 mm have been produced. We have also obtained a homogeneous mixture of nanocrystals embedded in a glassy matrix in both Cu- and Ni-based 4-mm rods. It is expected that in both these systems the glassy state can be obtained upon composition variation. Meanwhile, it is note-worthy that nanocrystalline alloys, whose recrystallization temperatures may exceed the crystallization temperatures of glasses, are important from the technology standpoint. Our systematic approach for forming bulk metallic glasses and nanocrystals is clearly working and many more bulk-sample forming systems can be expected in the future.

(4) Consolidation of amorphous powders obtained by mechanical alloying -

We have succeeded in amorphizing aluminum alloys by mechanical alloying. Amorphous $A\ell_{80}Ni_8Fe_4Gd_8$ quaternary powders are produced using the mechanical alloying (MA) technique, suggesting that powder metallurgy may be applied to the manufacture of aluminum metallic glasses as high strength, low density engineering materials. Detailed investigations into the microstructural evolution of the amorphous phase from elemental powders have been completed employing scanning and transmission electron microscopy as well as other analytical techniques. The results support previous observations of the amorphization reaction by interdiffusion developed from studies of simple binary alloy systems. The resulting amorphous powder demonstrates good thermal stability, and consolidated amorphous bulks up to 93% dense are easily produced. The final products are found to have mechanical properties resembling ceramics of the brittle type.

(5) Microstructure-mechanical property relationships -

We have been carrying out fundamental studies of new metallic glasses, on both their structure and microstructural effect on mechanical properties. Such studies are important because they can shed light on the origin of easy vitrification and superior mechanical properties. The latter refers to our earlier observation of significant enhancement in the tensile strength of Al-glass matrix with Al nanocrystallites embedded in it. Our result can be contrasted with the embrittlement of some metallic glasses when they are annealed. It has long been speculated that embrittlement results from some kind of structural change, which has not been confirmed. We have observed, for the first time, deformation-induced crystallization within the shear bands of some Al-glasses. F.c.c.-Al nanocrystalites are found exclusively within the shear band extending across the deformed ribbons. The nanocrystals can be produced by either bending or ball-milling. We conjecture that the deformation-induced structural change is due to local atomic rearrangements within the shear bands which exhibit enormous plastic strain. Furthermore, we find that the extent of atomic rearrangement depends on the short range order and chemical bonding strength of the amorphous state. From a technological viewpoint, this provides a means of forming nanocrystals where the formation of a product includes extrusion and some other type of deforming step.

Publications Resulting From ARO Contract No. DAAL03-91-G-0009 (only refereed articles are listed).

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- 12. Y. He, H. Chen, G.J. Shiflet, and S.J. Poon, "Studies of nucleation and growth in the crystallization of aluminum-glasses", in preparation.
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- 15. S.J. Poon, Y. He, G.J. Shiflet, and G.M. Dougherty, "Synthesis and Properties of Bulk Amorphous and Nanocrystalline Alloys", to be published in Conference Proceedings from NATO Conference on Science and Technology of Rapid Solidification and Processing.

- 16. G.J. Shiflet, Y. He, S.J. Poon, G.M. Dougherty, and H. Chen, "Aluminum-Rich Metallic Glasses", to be published in Conference Proceedings from NATO Conference on Science and Technology of Rapid Solidification and Processing.
- 17. Y. He, G.J. Shiflet, and S.J. Poon, "Formation and Properties of Light-Metal Amorphous Alloys", to be published in Proceedings of ARO Sagamore 40th Materials Research Conference.

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